

METC10 Desulfurization Sorbents for Low- and High-Temperature Applications

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Abstract

A series of novel, regenerable, desulfurization sorbents operational at wide range of temperatures (260 to 600 °C [500 to 1,100 °F]) has been developed by the in-house research staff at the U.S. Department of Energy's Federal Energy Technology Center. The sorbent, identified as METC10, has demonstrated extremely high attrition resistance as well as extremely high and stable reactivity under numerous testing regimes and both simulated and actual fuel-gas conditions. The METC10 sorbent is suitable for moving-bed reactor applications, and is the only sorbent that exceeded all the criteria required for use in the Tampa Electric Company (TECO) Clean Coal Technology (CCT) demonstration project. The sorbent was also tested at temperatures ranging from 260 °C (500 °F) to 370 °C (700 °F) with simulated coal gas. Even at these low temperatures, it was possible to achieve a sulfur loading of $>6.7 \text{ lb/ft}^3$, indicating that the sorbent is suitable for applications over a wide range of temperatures. It was also possible to prepare the METC10 sorbent for fluidized/transport reactor bed applications, using a spray-drying technique. These sorbents had high attrition resistance ($>95\%$) and high sulfur capacity ($>10 \text{ wt}\%$), and showed stable reactivity during muticycle testing.

Introduction

The U.S. Department of Energy's Federal Energy Technology Center (FETC) has funded research, development, and demonstration (RD&D) projects in advanced power generation for the last 20 to 25 years. The Integrated Gasification Combined-Cycle (IGCC) system has evolved as one of the more promising advanced power systems. It has been predicted that IGCC systems, with hot gas cleanup, will be able to offer significant improvements in environmental performance and overall plant efficiency compared to conventional pulverized coal-fired plants, which have efficiencies of 33 to 35 percent. It is expected that IGCC with hot gas cleanup will achieve efficiencies in excess of 52 percent and will be capable of producing power at a 20-percent lower cost of electricity than conventional coal-based systems. Furthermore, it is predicted that this increase in efficiency will be able to reduce CO_2 emissions by 35 percent.

Development of a suitable regenerable sorbent is one of the major barrier issues in the gas cleanup program for IGCC systems. The development of a regenerable sorbent has posed a challenging problem for the last 20 years (Lew et al. 1989), a challenge that had gone unmet until recently. Various formulations of zinc ferrite and zinc titanate in the form of extrudates and spherical pellets have been studied for removal of sulfurous gases from coal gasification streams at FETC and other facilities (Siriwardane and Poston 1990, 1993; Siriwardane, Grimm, et al. 1994; Siriwardane, Poston, et al. 1994). Problems of decrepitation, spalling, and loss of reactivity have occurred after multiple recycling between sulfidation and regeneration of these sorbents.

A series of novel sorbents containing zinc oxide were developed at FETC to address these problems (Siriwardane, Grimm, et al. 1994; Siriwardane, Poston, et al. 1994; Siriwardane 1996). These FETC developed sorbents showed superior performance during 20-cycle high-pressure fixed-bed tests with steam regeneration and a 50-cycle high-pressure fixed-bed test with dry regeneration. In addition, one of the FETC developed sorbents (METC10) was tested in the moving bed reactor at the General Electric (GE) pilot plant. Despite several operational problems at the facility, promising results were obtained during the testing. However, regeneration conditions at the GE pilot plant did not completely simulate the drastic regeneration conditions (10% SO₂, 482 to 510 °C at 5 to 7 atmospheres) encountered at TECO.

The METC10 sorbent was modified to obtain the necessary characteristics to withstand the drastic regeneration conditions encountered at TECO. This modified sorbent was named METC10-M. The modified sorbent was tested in a fixed bed for 25 sulfidation/regeneration cycles at Research Triangle Institute (RTI) under regeneration conditions that closely simulated those encountered at the TECO/CCT project (Turk and Gupta 1997; Siriwardane et al. 1998). The performance of the sorbent was excellent under these conditions, and it exceeded all the performance criteria required for the TECO/CCT project.

All previous tests with METC10 sorbents were conducted at temperatures higher than 482 °C (900 °F). Therefore, the METC10-M sorbent was tested at lower temperatures to determine whether it was suitable for low-temperature applications. The test results of these low-temperature studies are discussed in this paper.

In addition, a METC10-T sorbent suitable for use in fluidized/transport reactor beds was also tested in a bench-scale reactor. Superior attrition and sulfur capacity values were obtained for these sorbents. These promising results are also discussed in this paper.

Objectives

One of the objectives of this work is to determine whether the sorbent is suitable for low temperature (< 370 °C [700 °F]) applications. The sorbent should have a reasonable sulfur capacity (> 6 lb/ft³) while maintaining high mechanical strength and high attrition resistance at these low temperatures.

Another objective of this work is to prepare fluid/transport bed reactor sorbents suitable for the Pinon Pine/clean coal project (CCT). The fluid/transport bed sorbent should have an attrition value (measured using the ASTM three-hole attrition method) of less than 5 wt% and a sulfur absorption capacity greater than 6 wt%. The sorbent should be able to retain its sulfur capacity during multicycle testing.

Experimental

Low-Temperature Fixed-Bed Testing of METC10-M Sorbent at RTI

The METC10-M sorbent was developed by FETC in-house researchers. The parent version of this sorbent (METC10) was tested in General Electric's (GE's) pilot-plant facility in March 1996. The current version, designated METC10-M, was an improved version of the parent material. United Catalysts Inc. (UCI) prepared the current formulation under guidance from FETC using equipment large enough to produce a sorbent batch with the physical and chemical characteristics that would be obtained for a commercially prepared sorbent batch. This sorbent was supplied as 3-mm ellipsoidal pellets.

The low-temperature tests were conducted at RTI. Sulfidations were performed at 371, 343, 315, 288 and 260 °C (700, 650, 600, 550 and 500 °F) and 2,026.5 kPa (20 atm), utilizing simulated TECO coal gas (1.2% H₂S, 35.8% CO, 12.2% CO₂, 26.8% H₂, 18.1% H₂O, and 5.95% N₂). During regenerations, the temperature of the sorbent bed was maintained at 371 °C (700 °F). Regenerations were performed at 5 atm with 7% O₂ that was preheated at 538 to 566 °C (1,000 to 1,050 °F). Space velocities during sulfidation and regeneration were 2000 hr⁻¹ and 1000 hr⁻¹, respectively.

The sorbent was loaded only up to 6.7 lb/ft³ of sulfur at each temperature. A ten-cycle test was performed at 260 °C (500 °F). During the ten-cycle test, the sorbent was loaded up to 6.7 lb/ft³ at each cycle with the exception of the tenth sulfidation cycle, which was performed until breakthrough. Some of the sorbent was removed for analysis after the tenth sulfidation cycle. The remaining sorbent bed was regenerated. Physical and chemical analyses were performed with both sulfided and regenerated sorbents.

Fluid-Bed Testing of METC10-T Sorbent

A METC10-T sorbent suitable for fluid/transport reactor-bed testing was prepared, using a spray drying technique. This sorbent was tested in a bench-scale low-pressure fluid-bed reactor. Sulfidations were performed at 538 °C (1,000 °F) and 260 kPa (1 atm), using simulated KRW coal gas (47% nitrogen, 8% steam, 5% CO₂, 24% CO, and 14% H₂) with 2% H₂S. The superficial velocity for all sulfidations was 0.16 ft/sec. The outlet H₂S was monitored, using on-line mass spectrometry and gas chromatography. All dry regenerations in the low-pressure reactor were done at 260 kPa (1 atm) with 6% oxygen diluted with nitrogen at 538 °C (1,000 °F). The sorbent was loaded up to 6.7 wt% during sulfidations, but the last sulfidation cycle was conducted

until breakthrough. The sorbent was also tested at 315 °C (600 °F), using coal gas with a low reducing power (35.7% nitrogen, 31% steam, 2.4% CO₂, 19.8% CO, 1% CH₄ and 10% H₂).

Results

Low-Temperature Fixed-Bed Testing of METC10-M Sorbent at RTI

Scoping Tests of METC10-M. Initial scoping tests were conducted to identify the operational temperatures of the sorbent below 482 °C (900 °F). The sulfidation curves at 371, 343, 315, 288 and 260 °C (700, 650, 600, 550 and 500 °F) are shown in Figure 1. These tests confirmed that even at 260 °C (500 °F), the sorbent can be loaded up to 6.7 lb/ft³ while maintaining the hydrogen sulfide level below 20 ppm (no H₂S breakthrough).

Sulfidation Results of the Ten-Cycle Test at 260 °C (500 °F). Hydrogen sulfide concentration in the reactor effluent as a function of time is shown in Figure 2. The breakthrough time at the tenth cycle is about 160 minutes. This corresponds to a sulfur loading of about 9 to 10 wt%, which is greater than 6.7 lb/ft³ of sulfur. The pre-breakthrough H₂S levels were below 20 ppm for all 10 cycles. This indicates that the sorbent performs well even at 260 °C (500 °F) during multi-cycle testing.

Regeneration Results from the Ten-Cycle Test at 260 °C (500 °F). A typical temperature profile during regeneration is shown in Figure 3. The initial temperature of the reactor bed was at 371 °C (700 °F). The temperature of the preheated regeneration gas was 538 to 566 °C (1,000 to 1,050 °F). These results clearly indicate that the sorbent initiates regeneration at 371 °C (700 °F) with 7% O₂ at a space velocity of 1,000 h⁻¹. The peak temperature of the sorbent bed, caused by the exothermic reaction during regeneration, was 621 °C (1,150 °F). When the temperature of the reactor bed started to decrease below the peak temperature, the furnace temperature was increased from 371 °C (700 °F) to 593 °C (1,100 °F) to complete the regeneration. The regeneration performance of the sorbent was consistent during all the regeneration cycles.

Physical and Chemical Characterization of the Sorbent after the Ten-Cycle Test at 260 °C (500 °F). Various physical and chemical properties of fresh and reacted sorbent, removed at various stages, are shown in Table 1. The sulfur loading at breakthrough was 9.1 wt% after the ten-cycle test. The ASTM attrition of the fresh material was 0.5 wt% and it increased to 1.9 wt% after ten cycles. The crush strength of the ten-cycle sulfided material was 14.8 lb/pellet, compared to 5 lb/pellet for the fresh material. This indicated that the mechanical strength of the sorbent was excellent during the ten-cycle test at 260 °C (500 °F).

Table 1. Physical and Chemical Properties of Fresh and Reacted METC10-M Sorbent at 260 °C (500 °F).

Property	Fresh	After 10th sulfidation	After 10th regeneration
Measured sulfur loading at gas inlet (wt%)	NA	9.1	NA
ASTM attrition (wt%)	0.5	1.9	1.9
Crush strength (lb/pellet)	5	14.8	8.5

NA = Not applicable

Fluidized-Bed Testing of METC10-T Sorbent at FETC

The METC10 sorbent was prepared using a spray drying method. It was possible to prepare particles with average sizes of 65 μm (METC10-TS) and 140 μm (METC10-TL). The packing densities of these sorbents were in the range 0.9 to 1.07 g/cc.

Attrition values of these sorbents, after 5 hours and 20 hours, were less than 5 wt%, indicating that the attrition resistance values of both sorbents were excellent. TGA sulfur capacities of both sorbents after 9.5 cycles of testing also showed excellent results (Figure 4). Sulfur loading, measured after the bench-scale testing, further confirmed the high sulfur capacities of these sorbents, as shown in Table 2. The breakthrough time during the bench-scale fluidized-bed tests was higher at the tenth sulfidation cycle than at the fourth sulfidation cycle. This indicated that sorbent sulfur capacity is stable during multicycle tests.

Table 2. Physical and Chemical Properties of Fluidizable METC10 Sorbents

Property	METC10-TS	METC10-TL
ASTM attrition (wt%)		
5-hour loss	4.2	1.6
20-hour loss	4.9	3.0
Measured sulfur loading (LECO) after 9.5 cycles of TGA testing (wt%)	23	23
Measured sulfur loading (LECO) after bench-scale fluidized-bed testing (wt%)	19	22

When the sorbent was tested at 315 °C (600 °F), using coal gas with low reducing power (35.7% nitrogen, 31% steam, 2.4% CO₂, 19.8% CO, 1% CH₄ and 10% H₂), it was possible to obtain a sulfur loading of 10 wt% after 3.5 cycles. This indicates that the sorbent can be used at low temperatures even with a coal gas with low reducing power.

Summary and Conclusions

Based on fixed-bed testing of the METC10-M sorbent (suitable for either fixed-bed or moving-bed applications) at RTI, the following conclusions can be made:

- The sorbent is capable of absorbing 6.7 lb/ft³ of sulfur (at gas inlet) without H₂S breakthrough over a wide range of temperatures (260 to 600 °C [500 to 1,100 °F]).
- The pre-breakthrough H₂S concentration was below 20 ppmv during multi-cycle testing at both 482 °C (900 °F) and 260 °C (500 °F).
- Sulfur capacity was stable during multi-cycle tests at both 482 °C (900 °F) and 260 °C (500 °F). The sulfur capacities of the sorbent were 17 wt% and 9 wt% at 482 °C (900 °F) and 260 °C (500 °F), respectively.
- This sorbent can be easily regenerated at 482 to 510 °C (900 to 950 °F) with 3.5% O₂ at a space velocity of 2,000 h⁻¹. Regeneration can be initiated even at a 371 °C (700 °F) solid temperature with pre-heated oxygen (7%) at 566 °C (1,050 °F) and at a space velocity of 1000 h⁻¹.
- The sorbent was able to maintain its mechanical strength over ten cycles of testing 260 °C (500 °F). The crush strength of the pellets increased from 5 lb/pellet for the fresh to 14.8 lb/pellet for the ten-cycle sulfided material, while the ASTM attrition increased from 0.5 to 1.9 percent.

Based on the fluidized-bed testing of METC10 sorbent, the following conclusions can be made:

- Sorbents with an attrition resistance of >95 wt % can be prepared using a spray-drying technique.
- Both TGA and bench-scale studies indicated that the METC10 fluidized/transport bed sorbent has an excellent sulfur capacity.
- Stable sulfur capacity was observed during multi-cycle testing.

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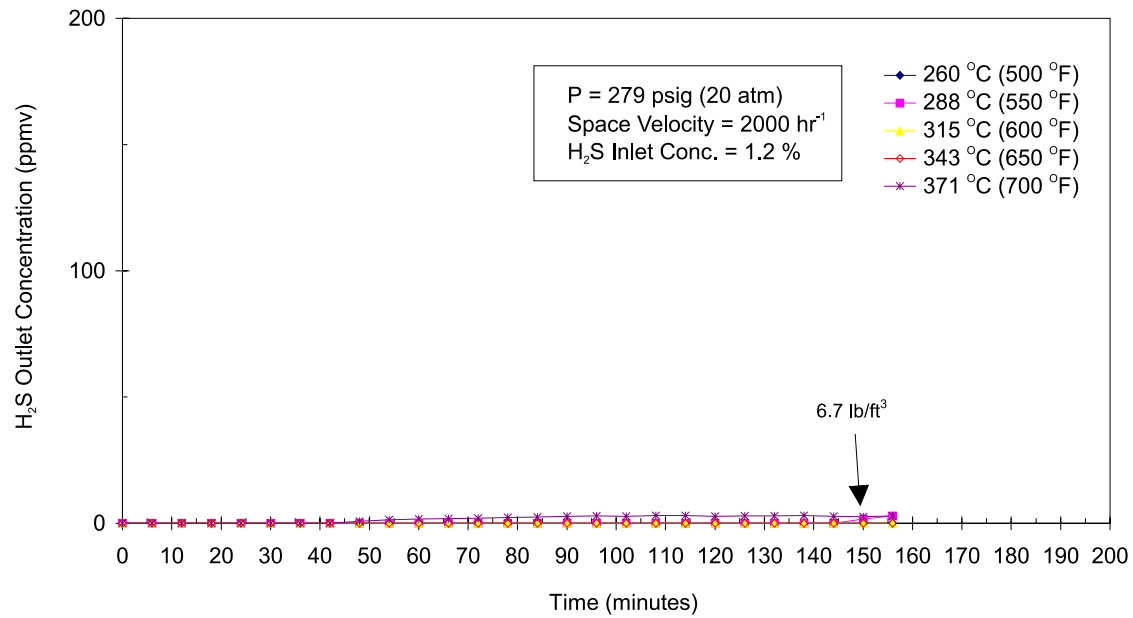


Figure 1. Sulfidations of METC10-M at 260 to 371 °C (500 to 700 °F)

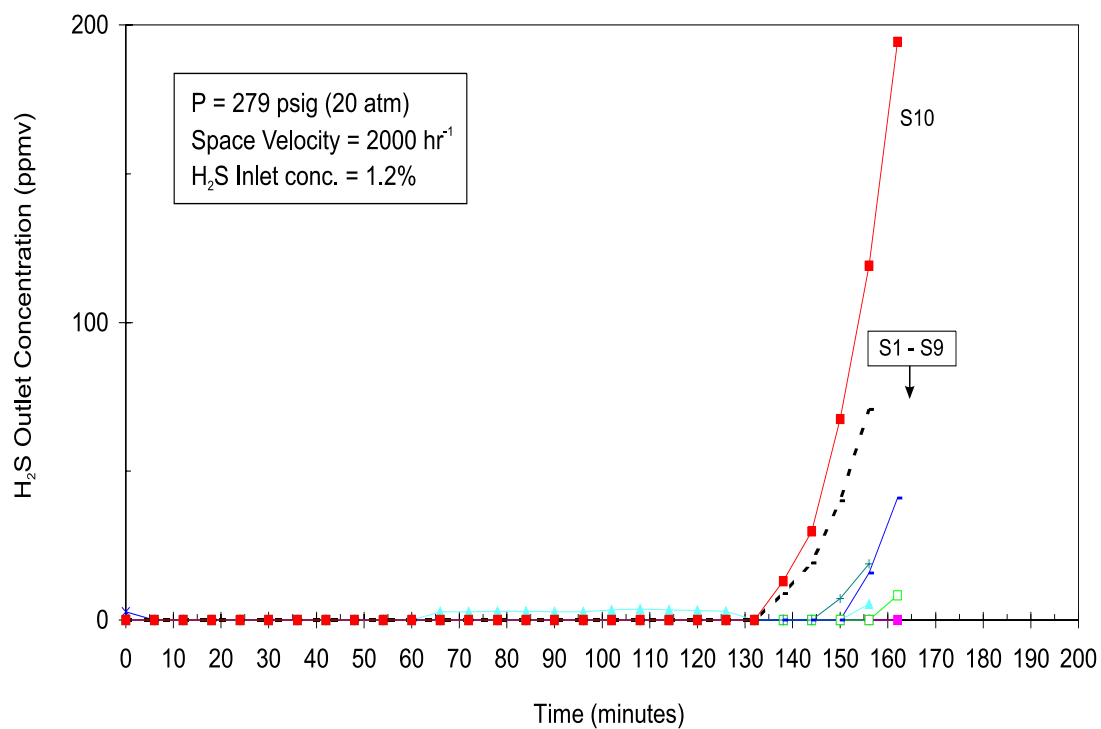


Figure 2. Sulfidations of METC10-M at 260 °C (500 °F), Ten-Cycle Test at RTI

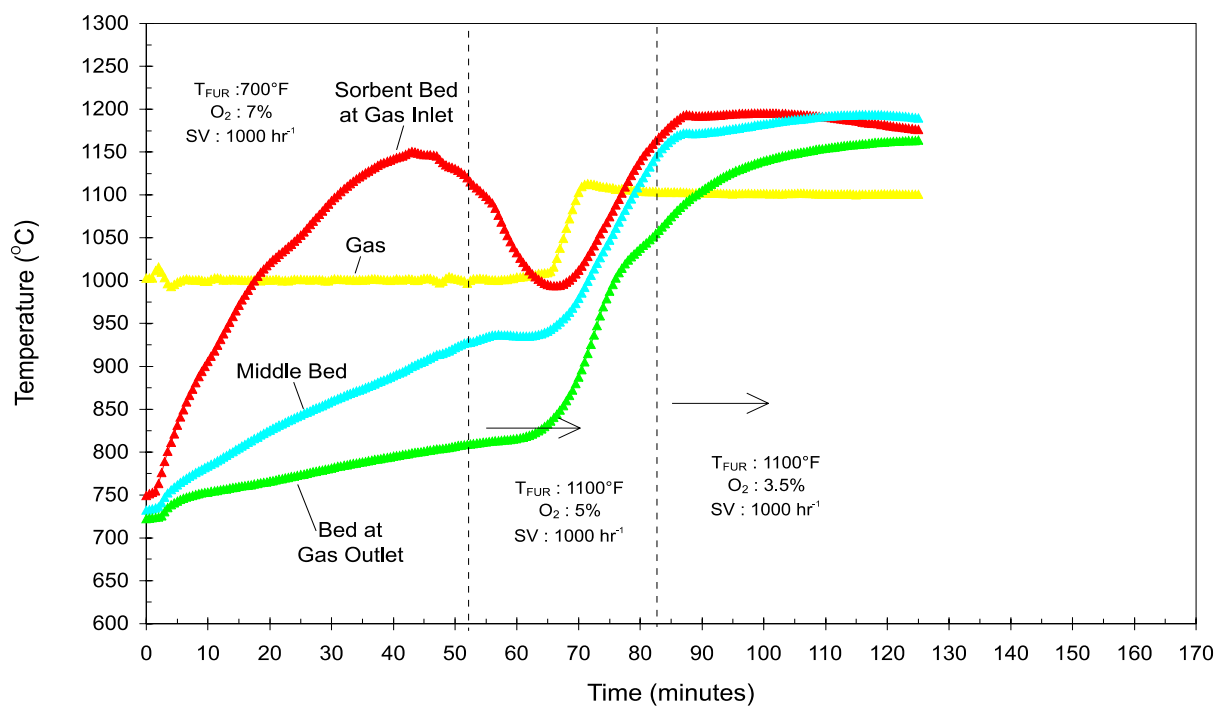


Figure 3. Regeneration of METC10-M Sorbent at 371 °C (700 °F)

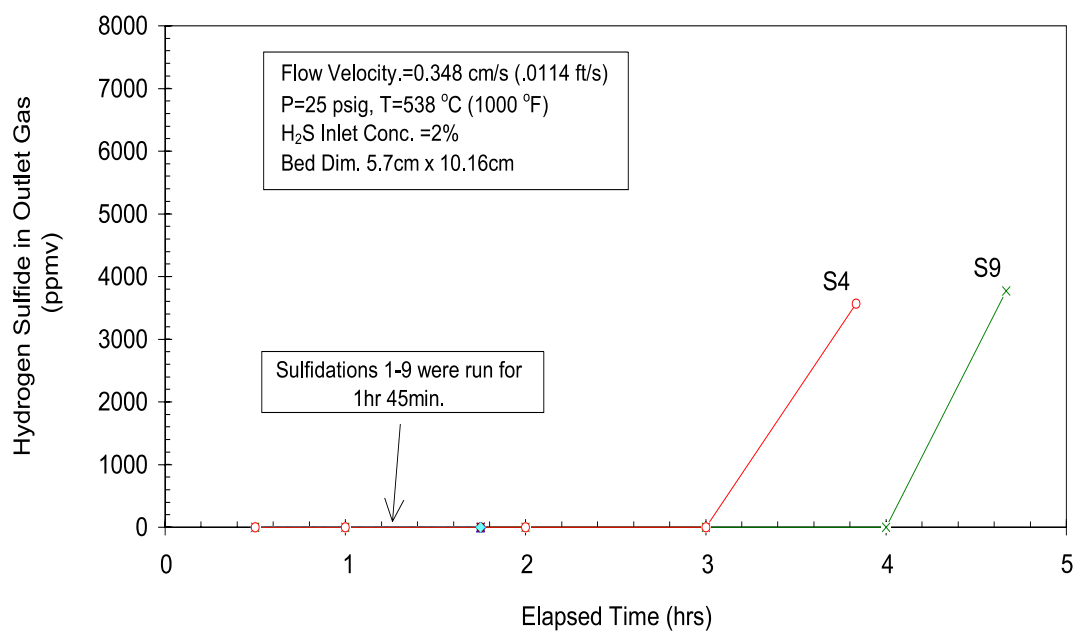


Figure 4. Sulfidations (9.5 Cycles) of METC10, Low-Pressure Fluid-Bed Tests